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The Determination Of Carbon in Steel

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THE DETERMINATION OF CARBON IN STEEL

BY

JOSEPH P. AUMER

THESIS

For the Degree of Bachelor of Science

in Chemistry

College of Science

University of Illinois

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

JOSEPH P. AUMER

ENTITLED THE DETERMINATION OF CARBON IN STEEL

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF Bachelor of Science in Chemistry

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THE DETERMINATION OF CARBON IN STEEL.

Among the many methods which have been proposed for the determination of carbon in iron and steel, two have been of special interest in the work taken up in this thesis. One of these is the direct combustion of the borings or drillings in a current of oxygen; the other, solution in copper potassium chloride and combustion of the residue.

Up to the year 1893 ammonium copper chloride had been extensively used for the solution of iron and steel in carbon determinations. It was found, however, a difficult matter to obtain this substance free from organic impurities. The American committees on the International Standards for the analysis of Iron and Steel, (Jour. Amer. Chem. Soc. 1893, p. 449), first called attention to important errors likely to occur by the use of this substance as a solvent, and stated that these errors were due to such impurities as pyridine and other tarry products. Copper potassium chloride was substituted in its place and found to be a complete remedy. They

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found, however, that,contrary to the usual practice, the solution must not be neutral, but acid with from five to ten per cent of hydrochloric acid. Attention was also called to the fact that chlorine compounds may pass from the combustion tube into the absorption train.

In the Journal of the American Chemical Society, 1900, p. 210, Geo. Wm. Sargent gives the following reactions for steel in an acid solution of copper potassium chloride:

$$Fe + CuCl_2 = FeCl_2 + Cu \text{ and}$$

$$Cu + CuCl_2 = Cu_2Cl_2$$

He attempts to oxidize the cuprous chloride with air, but finds the process to require too long a time. Oxidation with an electric current yields the cupric chloride at the expense of the hydrochloric acid. Chlorinating directly with chlorine proves satisfactory. The results obtained with fresh solution or the chlorinated varying only a few thousands of a per cent.

The process recommended by the American committees on the International Standards for the analysis of Iron and Steel was briefly as follows:

Three grams of steel were treated with 200 cc. of an acid solution of copper potassium chloride (300 grams per liter and 15 cc. of concentrated hydrochloric acid for each determination.) After complete solution the carbon residue was filtered on an asbestos lined per-

forated platinum boat, washed with hydrochloric acid, and then free of chlorides.

This residue was burned in a porcelain combustion tube containing several inches of copper oxide, together with a coil of silver foil. The oxygen used was purified by passing it over red hot copper oxide, through caustic potash solution, then over calcium chloride. The gases, on leaving the combustion tube, were purified from chlorine by passing through two U-tubes, one containing a solution of ferrous sulphate, the other, anhydrous copper sulphate. Moisture was removed with calcium chloride and the purified carbon dioxide absorbed in a bulb containing caustic potash solution, and provided with a calcium chloride tube, to prevent escape of moisture. From six analyses made according to this method, the following results were reported, expressed in terms of carbon per cent.

1.050 1.057 1.054 1.030 1.054 1.053

In the Journal of the American Chemical Society, 1893, p. 526, C. B. Dudley and F. N. Pease give a detailed description of the same method with a few changes in the purifying train. An absorption tube containing silver sulphate solution is placed after the ferrous sulphate tube, to insure complete absorption of chlorine and hydrochloric acid.

In the Journal of the American Chemical Society,

1896, p. 1087, E. S. Summers states that the old combustion, although accurate, requires more time than can usually be spared,if a porcelain or glass tube is used. A series of results obtained by the chromic acid method were unsatisfactory, the samples containing a large amount of graphite yielding low results in carbon.

To avoid these errors, he made use of a platinum tube provided with coolers to protect the stoppers. The hot gases passing through the tube were cooled by means of a funnel shaped device filled with asbestos and attached to a glass tube,over which the stopper was fitted. By means of this apparatus, high carbon residues were burned in twenty minutes.

In the Journal of the American Chemical Society, 1898, p. 243, Geo. Auchy states that the wet combustion works faultily in the following particulars:

1. The potash bulbs do not absorb all of the carbon dioxide.

2. The prolong containing calcium chloride may not absorb all the moisture carried over from the potash solution.

3. The proportion of moisture escaping from the prolong is not uniform.

4. The potash solution may lose something besides moisture.

5. Some chloro chromic compounds, other than those absorbed by Prof. Langley's "pyro" mixture may sometimes form and cause high results.

The wet combustion method to which Geo. Auchy refers is given in Blair's Chemical Analysis of Iron and Steel, and is briefly stated as follows:

The apparatus consists of a round bottom flask closed by a stopper having two holes. Into one of these a glass stopper funnel is fitted, into the other, a water jacketed glass tube. The latter is connected to a purifying train of anhydrous copper sulphate, and calcium chloride, and a Liebig bulb containing potash solution, with its safety for carbon dioxide absorption. Three solutions are used.

1. A saturated solution of copper sulphate.

2. A solution of chromic acid containing one gram per cc.

3. A mixture of sulphuric, phosphoric, and chromic acid made up as follows:

Solution (2)----------35 cc.

Concentrated sulphuric acid----------750 cc.

Phosphoric Acid, specific gravity,1.40-340 cc.

Water----------190

One gram of drillings is placed into the flask, the stopper put into place, and a current of water

started through the condenser. Fifteen cc. of solution(1) are poured through the funnel and left in contact with the drillings until a coating of copper is formed upon them. 15 cc. of solution(2) and 135 cc. of solution (3) are added and solution brought slowly to boiling. Carbon is oxidized to carbon dioxide, which is purified and then absorbed in the Liebig bulb.

The first error was remedied by the use of two potassium hydroxide bulbs, each provided with a prolong containing calcium chloride. By increasing the specific gravity of the potassium hydroxide solution from 1.27 to 1.40, the amount of carbon dioxide in the second bulb was greatly reduced, in some instances eliminated, and the absorption found much more satisfactory. The increase of the potash bulbs,found by a blank determination, was thought to be due to moisture escaping the drying train,and the slight increase in weight of the second bulb due to moisture carried over from the first.

That the amount of moisture escaping the potash bulbs is not uniform, was shown in a large number of determinations, in which the bulbs were followed by a weighed sulphuric acid tube. The amounts of moisture absorbed by the latter varied from .006 to .138, expressed in terms of carbon per cent.

It was also found that freshly prepared caustic potash bulbs suffer a loss in weight, due to something

beside moisture, if air is not aspirated through them before using. In some instances results came out too high,for which no explanation could be given, unless some chloro chrom compounds passed through the purifying train.

P. W. Shimer,(Jour. Amer. Chem. Soc., 1899, p.561) proposes the use of a platinum crucible provided with a water cooled stopper, in place of a combustion tube. The gases were passed from this into a copper tube containing copper oxide heated to redness. Hydrochloric acid and chlorine were absorbed by means of distilled water in an absorption tube containing glass beads, and kept cool by a wick wrapped about it, and hanging into a beaker containing distilled water. The steel was dissolved in copper potassium chloride solution. Blank determinations,obtained by forcing air through the apparatus, gave an increase in weight of .0005 grams, while, by drawing air through, an increase of from .0007 to .0018 grams was obtained. Without the copper oxide tube, results came out low. When copper oxide covered asbestos was placed in the crucible, the results were higher, still, however, not high enough. Results obtained by this method vary within less than .01 per cent carbon.

In the Journal of the American Chemical Society, 1900, p. 277, Geo. Wm. Sargent, in a second article, gives a detailed description of an apparatus used by

him for carbon in steel. Beside the purifying train, furnace and absorption train, he introduces a platinum spiral tube as preheater and a similar cooled copper spiral, to cool the gases. Hydrochloric acid and chlorine are absorbed in a tube containing wet sand. The carbon residue is obtained by the standard solution method, burned in oxygen and the latter removed with air. The rate of aspiration is quite rapid, from four to five bubbles per second. No loss in weight of the potash bulbs is caused by the rapid flow of gas. This is thought to be due to the presence of the cooler, gases entering and leaving bulbs at the same temperature, having less tendency to absorb or deposit moisture. Results by this method compared with those obtained by the use of a platinum tube vary less than .01 per cent.

In the Journal of the American Chemical Society, 1900, p. 334, Geo. Auchy states that the following method for carbon, given in Blair's Chemical Analysis of Iron and Steel, is known to be inexact. The following statements are taken from Blair.

The carbonaceous residue may also be weighed directly, instead of being burned. In this method, filter on a Gooch crucible, dry at 100 degrees C., and weigh. Burn off the carbonaceous matter and weigh the residue; the difference between the two weights is carbonaceous matter, which contains about 70 per cent of carbon in

steel or iron free from graphite. This method of direct weighing is applicable only to samples when all the carbon is in the so-called combined condition.

George Dougherty, in the Iron Age, May 11, 1899, also Chemical News, 1899, p. 121, proposes the following method for carbon in iron and steel.

Dissolve the steel in a 33 per cent solution of copper potassium chloride. Warm slightly and stir frequently to aid the solution of precipitated copper. Filter the residue remaining on a weighed Gooch crucible provided with an ashless paper disc. Wash twice with dilute hydrochloric acid and water, then with hot nitric acid, (specific gravity, 1.135) and water. Dry the crucible and contents at 120 degrees C. and weigh. The loss upon ignition represents graphite and organic compound. By subtracting from this weight the graphite elsewhere determined, gives the organic compound, which, when multiplied by the factor .675, gives combined carbon.

Auchy has shown, by a number of determinations, that hot nitric acid of the specific gravity stated, dissolves some of the carbon and that some of the acid remains in the residue. He states, likewise, that the apparent loss of carbon dioxide due to loss of moisture from potash bulbs, is due to an imperfect passage of gases through the absorption train, that both hydrochloric acid and sulphur dioxide pass from the combustion tube, that the heating of the double chloride solution may

cause loss of carbon.

In this same article, attention is also called to the difference between the absorption trains used by Dr. P. W. Shimer and Prof. Arnold in his book,"Steel Works Analysis." The former uses water for the absorption of hydrochloric acid and chlorine, and calcium chloride for drying. The latter, chromic acid for sulphur dioxide absorption, and concentrated sulphuric for drying.

The former purifying chain is based upon the belief generally prevalent among American chemists, that hydrochloric acid and chlorine, if present in the carbon sponge, are not absorbed by the copper oxide, but pass out of the combustion tube, while sulphur dioxide is believed to be converted into sulphur trioxide in the presence of the glowing copper oxide, and absorbed by it. Prof. Arnold's belief is the exact opposite to this, namely, that hydrochloric acid and chlorine are absorbed by the copper oxide and that sulphur dioxide escapes unchanged. That chlorine or hydrochloric acid do leave the combustion tube, was shown by testing the water of the Shimer apparatus, after making a number of combustions. On the other hand, as proof that sulphur dioxide passes out of the combustion tube, Arnold mentions an experiment in which potassium permanganate solution placed after the combustion tube and connected with it,

became decolorized by the gas. Auchy, himself, finds that chromic acid solution is reduced, but that the reduction is due to hydrochloric acid and not to sulphur dioxide, since the reduction does not take place when the chromic acid is preceded by a tube containing water.

In the same volume, p. 791, Robert Job and Charles T. Davies state that after giving Dr. Sargent's apparatus a thorough trial, they came to the conclusion that it could be reduced to much simpler form without impairing the accuracy of the results. By lengthening the combustion tube, the copper tube containing copper oxide could be eliminated, likewise, the copper spiral for cooling the gases. That moist sand does not completely absorb hydrochloric acid and chlorine, and replace it by an absorption tube containing anhydrous copper sulphate and cuprous chloride and inserting beyond this a second tube containing sulphuric acid and silver sulphate. The commercial oxygen used by them gave a blank of .2 mg.

In the Journal of the American Chemical Society, 1902, p. 1206, George Auchy states that too rapid a flow of gas causes a loss of carbon dioxide due to incomplete oxidation by the copper oxide. He uses copper oxide in a crucible instead of in a combustion tube. He also finds that at least some of the hydrochloric acid and chlorine are retained by the copper oxide.

In an article signed J. T., published in the Chemical News, 1903, p. 65, it is stated that the usual method for carbon by dissolving the steel in a double copper salt and burning of the carbon residue, cannot be applied to high-speed self-hardsteels recently introduced. The results are from .05 to .10 per cent low when compared with those obtained by direct ignition with red lead. These results have been explained by the assumption that during solution, a part of the metallic carbides were dissolved, passing from the solution as hydrocarbons.

The writer of this article, however, found;(1) That no hydrocarbons were given off during solution; (2) That the residual carbides contain all the carbon present in the steel, but the unusual amount of chromium and tungsten,also in the residue, prevent the carbon from being entirely burned, except at very high temperatures, or after mixing with an oxidizing reagent. That carbon remained in the residues was found by grinding these and burning them a second time. The total weight of carbon dioxide obtained by two ignitions agreed with that obtained by ignition with red lead.

Charles M. Johnson (Jour. Amer. Chem. Soc., 1906, p. 862) states that in making duplicate analyses by dissolving steel containing large amounts of chromium, tungsten or molybdenum in copper potassium chloride solution, duplicate results fail to agree. He believes

this variation to be due to loss of carbon as hydrocarbons.

His purifying train differs from those previously mentioned, in the use of granulated zinc for the removal of hydrochloric acid and chlorine and phosphoric anhydride, in place of calcium chloride. By varying the acidity of the solution, it was found that the more strongly acid solution gave the highest results as well as the lowest. Those stirred for a short time gave higher results than those of longer stirring. Those carbon residues through which air had been drawn for any considerable length of time came out low.

To avoid the errors of the solution method, he proposes to burn the steel directly with red lead. Two grams of the steel borings are mixed with four grams of red lead and burned in a porcelain tube provided with copper oxide, in a current of oxygen. The carbon dioxide is absorbed in a special caustic potash bottle designed by the experimenter. Two of these are prepared, one being used as a tare. The per cent of carbon in the litharge is determined by absorption of carbon dioxide in barium hydroxide. The barium carbonate formed is washed and weighed. The per cents of carbon found by this method agree with those obtained by absorption in caustic potash, but is preferred because it is more rapid. The results obtained differ from those by solution in copper potassium chloride

from .003 to .02 per cent. Accurate results were also obtained by use of red lead alone, omitting the copper oxide.

The most recent work published upon carbon in iron and steel appeared in the Journal of the American Chemical Society, May, 1908, p. 773. C. M. Johnson gives a detailed description of a combustion furnace heated by electricity. It consists of a steel tube containing a non-conducting packing of magnesia surrounding a smaller quartz tube wound with Hoskin's wire, in which the iron or steel is burned. The combustion takes place in a current of purified oxygen, with or without red lead, depending upon the composition of the sample.

The most important difficulties encountered in determining carbon in steel by the solution method are; (1) Too much time is required for a single determination; (2) It cannot be used for steels containing unusually large amounts of chromium, tungsten or molybdenum; (3) Some carbon may be lost by oxidation during solution of the steel.

A good method for the determination of carbon in steel should be rapid and give accurate results for all varieties of steel. The apparatus required should be simple and durable. The direct combustion method fulfills these conditions more closely than any of the

other methods proposed, and it is, therefore, desirable that it should be more extensively developed.

EXPERIMENTAL.

The purpose of the laboratory work was to compare the solution method in copper potassium chloride with the direct combustion method and to discover and remedy, if possible, any discrepancies found.

Experiments were first made upon a sample of Bessemer steel, marked 60, determining carbon by the solution method. The solvent was prepared by dissolving 300 grams of copper potassium chloride in 1 liter of water and filtering through asbestos. Three grams of steel were dissolved in 200 cc. of this solution, to which 15 cc. of concentrated hydrochloric acid had been added. The mixture was stirred continually by a stirring machine, until all the steel and precipitated copper had dissolved. The solution was filtered on an asbestos filter, the carbon residue washed three times with hydrochloric acid, then free from chlorides, transferred to a porcelain boat and dried in an oven for one hour at 100 degrees C.

The combustion apparatus consisted of a combination soda lime and sulphuric acid purifying jar, (Benedict's Elementary Organic Analysis, p. 14), a Jena glass combustion tube provided with a two inch copper plug and five inches of copper oxide held in place by two half-inch copper plugs, with a space be-

tween for a boat. The purifying train beyond the combustion tube consisted of a calcium chloride tube and an anhydrous copper sulphate tube. The carbon dioxide was absorbed by means of soda lime prepared as directed, in Benedict's Elementary Organic Analysis, p. 32. Two U-tubes were filled with this, two others filled half with soda lime and half with calcium chloride; the two separated by a glass wool plug. These were placed alternately in the absorption train, one of each being used as tare.

Three samples of about 3 grams each were dissolved and treated as stated above, and burned in the furnace. Taking into account a blank determination, the following results were obtained for carbon:

.488 per cent .471 per cent .466 per cent.

No precaution had, however, been taken to absorb sulphur. By absorption of the latter in an acid solution of barium chromate, the following results were obtained:

No.	Per cent Carbon
69	.434
70	.473
72	.449

In making determinations 69 and 72, a platinized asbestos preheater was placed before the barium chromate tube. In No. 70 this was omitted and some

sulphur dioxide not absorbed by the barium chromate may have passed into the soda lime tubes. No's 69 and 72, however, are much lower, showing that sulphur dioxide passes out of the combustion tube from the carbon residue.

Direct Combustions.

The apparatus used for direct combustion work consisted of a platinized asbestos preheater, two gas wash bottles containing 1:1 caustic potash solution and a calcium chloride jar. The combustions were made in a platinum tube, the ends of which were cooled by lead pipe coils, through which water circulated. The hot gases were cooled by four perforated porcelain discs, two toward each end of the tube. The purifying train beyond the platinum tube consisted of a second preheater, a U-tube containing an acid solution of barium chromate, an anhydrous copper sulphate and calcium chloride tube.

The steel to be burned is placed into a porcelain boat containing a layer of alumina and transferred to the center of the platinum tube, porcelain discs and stoppers are arranged, also weighed soda-lime tubes. A current of oxygen, from one to two bubbles per second, is started through the apparatus and the central portion of the tube heated to redness with a blast lamp.

The results obtained are given below and show great variation, due to slight decomposition of rubber stoppers, improper absorption of carbon dioxide, and slight impurities in the alumina.

No.	Direct Weight	With tare.
12	.441	.420
13	.420	.343
15	.394	.382
16	.324	.313
17	.300	.393
20	.357	.353
21	.360	.333
24	----	.510

The figures express per cent of carbon. Improper absorption by tubes was descovered by taking the direct weight of the first soda lime tube and its safety as well as against a tare.

That the combustion was incomplete was shown by the following experiment. The residues from 16, 20 and 21 were ground in a steel mortar. The magnetic oxide of iron, thus reduced to a fine powder, was removed by passing through a fine sieve and the remaining sample dissolved by the standard solution method and burned in the furnace. The residue was found to contain .00758 grams or .126 per cent of carbon.

In order to avoid further errors with the platinum tube arrangement, we were provided with a Gooch platinum combustion crucible. This consisted of two parts so arranged that the cover could be sealed on with sodium tungstate. A combustion with this apparatus was carried out as follows:

A small pail made of platinum foil and somewhat smaller than the interior of the crucible, was filled with ignited and finely powdered alumina. With a stirring rod, a hole was made into this large enough to hold two grams of steel. The pail was placed into the crucible upon a layer of alumina, the cover put into place and sealed, and a current of oxygen passed through the apparatus. The lower portion of the crucible was kept at red heat for thirty-five minutes. The blast was then removed and air passed through the apparatus for ten minutes. From the increase in weight of the tubes, the following percentages of carbon were calculated:

No.	Per cent Carbon
26	.417
27	.483
28	.446
29	.510

Since practically all errors had now been removed with exception of small impurities in the alumina,

still further attention was given to this. A fresh portion was ignited until repeated weighings and ignitions gave practically no change in weight. With this alumina, thirty-five minute combustions gave the following results:

No.	Per cent Carbon
31	.439
33	.446

The time of heating was then reduced to twenty minutes, which gave a result of .443 per cent carbon. Other results obtained by still further reducing the time of heating are given below.

No.	Per cent Carbon	Time of Heating
35	.309	13
36	.428	12
37	.450	15
38	.443	15
39	.448	15
40	.469	15
42	.361	15
43	.470	15
46	.455	15

It is shown by these results that the combustion is incomplete if the sample is heated for less than fifteen minutes.

In order to determine if carbon was being com-

pletely burned, the residues from numbers 31, 33, 34, 37, 38 and 39, which had given the most closely agreeing results, were analyzed for carbon, and found to contain .00215 grams or .018 per cent of the original twelve grams.

Samples No. 40 and 43, given in the table, gave somewhat higher results and it was thought that the combustion had been more complete. Upon an examination of these residues, however, they were found to contain a slightly higher percentage of carbon, .020, which shows the error to be due to something else.

A more refractory sample, an open hearth steel, was next taken for experiment. By the solution method this gave the following results:

.257 per cent .258 per cent .251 per cent

By burning two duplicate samples of two grams each of the same steel in the crucible with Al_2O_3,.267 and .267 per cent carbon were obtained.

The results obtained from both steel samples are lower in carbon bythe solution method than by the direct combustion method. In the Journal of the American Chemical Society, 1906, p.862, C. M. Johnson states that duplicate results obtained by the solution method fail to agree, and that the loss is due to hydrocarbons passing from the solution. To determine whether any carbon was being lost as hydrocarbons, the following ex-

periment was carried out. Three grams of steel, 200 cc. copper potassium chloride solution and 15 cc. of concentrated hydrochloric acid were placed into a gas purifying bottle. This was connected with the furnace so that any gases passing from the solution would be burned in the furnace and the carbon dioxide absorbed by the soda lime tubes. Precaution was taken to absorb all hydrochloric acid, chlorine, sulphur and moisture. The solution was slightly stirred up by the air, but, to hasten the solution, the jar was occassionally shaken. The combustion was continued for three hours, giving an increase in weight of .0026 grams. A blank determination under similar conditions gave .0007 grams.

The steel had, however, at the end of this time not completely dissolved. It was transferred to a beaker and the solution continued by aid of the stirring machine. The residue contained .478 per cent C.

The conclusions drawn from the experiments performed were as follows:

1. The results obtained with the standard solution method for carbon in steel are lower than those obtained by the direct combustion method in Al_2O_3.

2. These low results are due to loss of carbon as hydrocarbons.

3. The residues obtained by the direct combustion method still contain a small amount of carbon.

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